3.7 Quantum Well

3.7.1. Application of Schroedinger Equation to Infinite Potential Well

Let us now discuss the problem of quantum confinement along one direction. It is same as the problem of particle in one dimensional box. In a quantum well (2D structure), particles are confined to a thin sheet of thickness 'a' along the x direction by infinite potential barriers, which create a quantum well as shown in fig. 3.10.

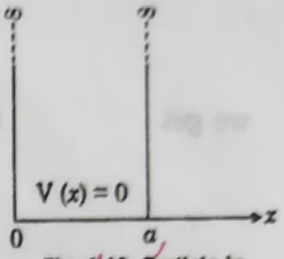


Fig. 3.10. Particle in infinitely deep potential well

In real systems, this confinement is due to electrostatic potentials (generated by external electrodes, doping, strain, impurities etc.); the presence of interfaces between different materials; the presence of surfaces; or a combination of these agents.

The potential function is

$$V(x) = \begin{cases} 0, & \text{for } 0 < x < a \\ \infty, & \text{for } x \le 0 \text{ or } x \ge a \end{cases} \quad \ldots (1)$$

The Schroedinger equation in the potential well region where $V(x) = 0$, is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

or $$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

or $$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \ldots (2), \quad k^2 = \frac{2mE}{\hbar^2}.$$

The boundary conditions are

$$\psi(0) = \psi(a) = 0 \quad \ldots (3)$$

The solution of equation (2) can be written as

$$\psi(x) = A\sin kx + B\cos kx \quad \ldots (4)$$

Applying $\psi(0) = 0$, we get $B = 0$. So

$$\psi(x) = A\sin kx$$

Now $\psi(a) = 0$ gives, $A\sin ka = 0$

or $$\sin ka = 0 = \sin n\pi \qquad \because A \neq 0$$

or $$ka = n\pi, \quad n = 1, 2, 3, \ldots$$

or $$k = \frac{n\pi}{a}$$

Thus, the solution of eqn. (2) is

$$\psi(x) = A \sin \frac{n\pi}{a} x$$

Applying the normalization condition of wave function

$$\int_0^a \psi^* \psi \, dx = 1,$$

we get $$A = \sqrt{\frac{2}{a}}$$

$\therefore$ $$\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \quad \ldots (6)$$

represents normalized eigen functions of the particle inside the well.

Also, $$k^2 = \frac{2mE}{\hbar^2},$$

or $$\frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

or $$E_n = E = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2} \quad \ldots (7)$$

are the discrete energy states of the particle within the quantum well region. However, outside the well region particle energies are continuous. Here n is called the principal quantum number.

$$E_{(n+1)} - E_n = \frac{\{(n+1)^2 - n^2\}\pi^2\hbar^2}{2ma^2} = \frac{(2n+1)\pi^2\hbar^2}{2ma^2}$$

or $$(E_{(n+1)} - E_n) \propto \frac{1}{a^2} \quad \text{and} \quad \propto (2n+1)$$

As the dimension $(= a)$ of the energy well increases, the spacing between discrete energy levels decreases. In the infinite crystal (i.e., bulk), a continuum occurs.

Above analysis shows that confinement of particle motion leads to discreteness or quantization of particle energies. The spacings between energy levels increases as principal quantum number n increases.

Zero Point Energy

The lowest energy (for $n = 1$) in the above case is

$$E_0 = \frac{\pi^2\hbar^2}{2ma^2} \neq 0$$

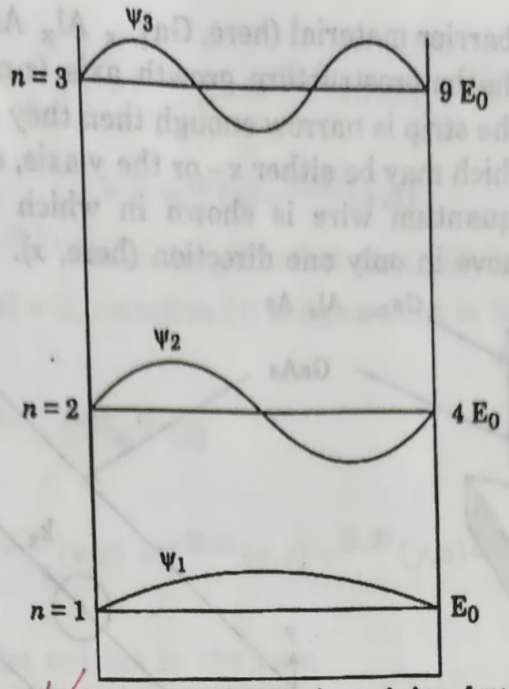


Fig. 3.11. First three eigen energies and eigen functions

This energy E_0 is called the zero-point energy or confinement energy. Its origin lies in the Heisenberg's uncertainty principle. Since the particle is constrained within a finite region, the variability in its position has an upper bound *i.e.* uncertainty in its position is finite whose maximum value can be 'a'. Therefore uncertainty in particle's momentum cannot be zero, the particle must contain some energy in this lowest state. The zero point energy increases with decrease in the width of the well.

3.8. QUANTUM WIRES

It is a one-dimensional nanostructure in which there is confinement along two dimensions and only one dimension is free for motion of charge carriers. A quantum wire or nanowire can be obtained from a quantum well by the process of lithography.

A standard quantum well layer can be fabricated by the process of photolithography or electron beam lithography and chemically etched to leave a free standing strip of quantum well material; the latter may or may not be filled in with

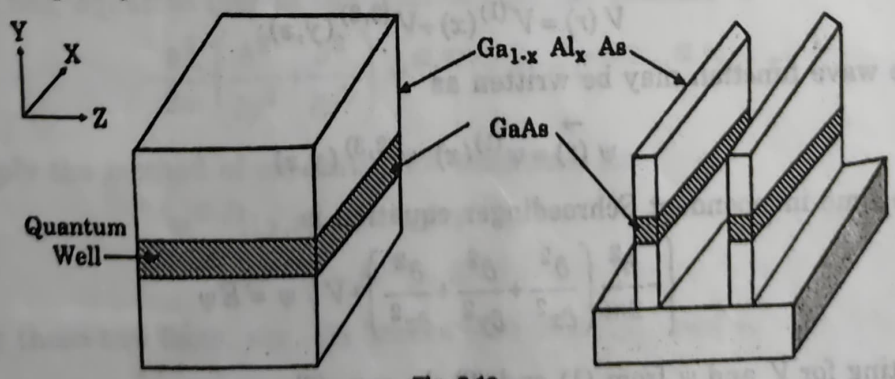


Fig. 3.12.

an overgrowth of the barrier material (here, Ga_{1-x} Al_x As). Any charge carriers are still confined along the heterostructure growth axis (z-axis), as they were in the quantum well, but if the strip is narrow enough then they are also confined along an additional direction which may be either x- or the y-axis, depending on lithography. In the Fig. 3.13. a quantum wire is shown in which the electron (or hole) is delocalized (free) to move in only one direction (here, x).

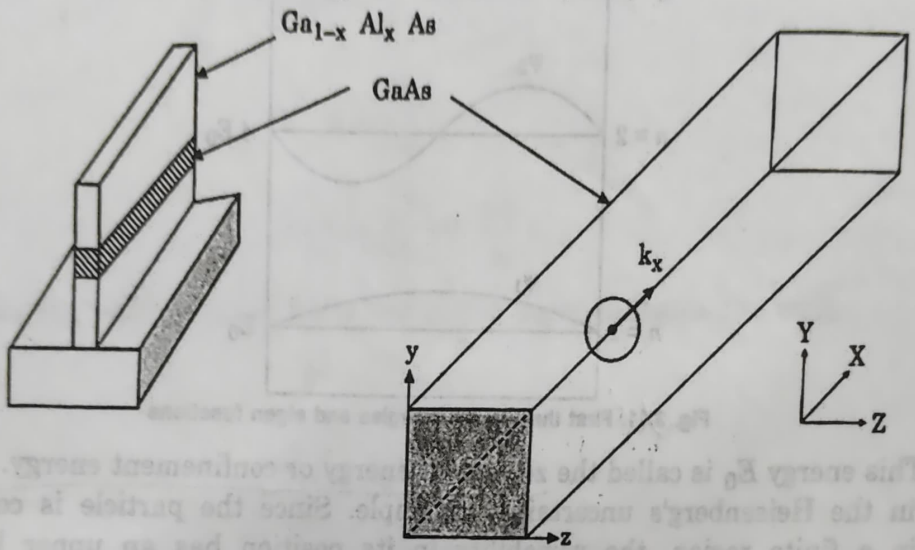


Fig. 3.13.

3.8.1. Application of Schroedinger Equation to the Problem of Particle in 2D Box

The problem of a quantum wire is analogous to the particle in two dimensional box problem from the confinement point of view. Let us consider a two-dimensional box as shown in Fig. 3.14. Let confinement is along y- and z-directions and the motion of the charge carrier is free along x-direction.

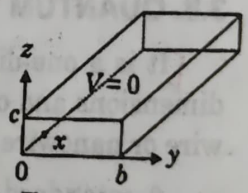


Fig. 3.14. Particle in 2D Box

The potential $V(\vec{r})$ is written as the sum of a two dimensional confinement potential (in the yz plane) plus a potential along the wire (*i.e.*, along x-axis) as

$$V(\vec{r}) = V^{(1)}(x) + V^{(2,3)}(y,z) \quad \text{... (1)}$$

The wave function may be written as

$$\psi(\vec{r}) = \psi^{(1)}(x)\ \psi^{(2,3)}(y,z) \quad \text{... (2)}$$

The time independent Schroedinger equation is

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right\}\psi = E\psi \quad \text{... (3)}$$

Putting for V and ψ from (1) and (2), in eqn. (3), we get

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V^{(1)}(x)+V^{(2,3)}(y,z)\right\}\psi^{(1)}(x)\,\psi^{(2,3)}(y,z)$$

$$=E\,\psi^{(1)}(x)\,\psi^{(2,3)}(y,z) \quad \ldots (4)$$

Writing $E=E^{(1)}+E^{(2,3)}$ and noting the fact that potential is zero everywhere inside the box (*i.e.*, $V^{(1)}(x)=0$), equation (4) is equivalent to two equations which are as follows :

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(1)}(x)}{dx^2}=E^{(1)}\psi^{(1)}(x) \quad \ldots (5a)$$

and $$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi^{(2,3)}(y,z)+V^{(2,3)}(y,z)\,\psi^{(2,3)}(y,z)=E^{(2,3)}\psi^{(2,3)}(y,z) \quad \ldots (5b)$$

Equation (5a) may be written in the form

$$\frac{d^2\psi^{(1)}(x)}{dx^2}+k_x^2\psi^{(1)}(x)=0, \quad \ldots (6), \qquad k_x^2=\frac{2mE^{(1)}}{\hbar^2}$$

It has plane wave solution given by

$$\psi^{(1)}(x)\approx\exp(i\,k_x\,x)$$

where k_x is the particle momentum along x-direction in which it is free to move with energy

$$E^{(1)}=\frac{\hbar^2\,k_x^2}{2m} \quad \ldots (7)$$

Now to solve equation (5b), the potential $V^{(2,3)}(y,z)$ has the form

$$V^{(2,3)}(y,z)=\begin{cases}0 & \text{when } 0<y<b \text{ and } 0<z<c\\ \infty & \text{otherwise}\end{cases} \quad \ldots (8)$$

Outside the box, $\psi^{(2,3)}(y,z)=0$ because particle cannot be outside it. Thus, within the box, equation (5b) in the light of eqn. (8), reduces to

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi^{(2,3)}(y,z)=E^{(2,3)}\psi^{(2,3)}(y,z) \quad \ldots (9)$$

To apply the method of separation of variables, let

$$\psi^{(2,3)}(y,z)=\psi^{(2)}(y)\,\psi^{(3)}(z)$$

$$E^{(2,3)}=E^{(2)}+E^{(3)}$$

Using these two facts, eqn. (9) breaks into two equations as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(2)}(y)}{dy^2} = E^{(2)}\psi^{(2)}(y) \quad \ldots (10a)$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(3)}(z)}{dz^2} = E^{(3)}\psi^{(3)}(z) \quad \ldots (10b)$$

These equations may be written as

$$\frac{d^2\psi^2(y)}{dy^2} + k_y^2\psi^2(y) = 0 \quad \ldots(11a); \quad k_y^2 = \frac{2mE^{(2)}}{\hbar^2}$$

and

$$\frac{d^2\psi^3(z)}{dz^2} + k_z^2\psi^3(z) = 0 \quad \ldots(11b); \quad k_z^2 = \frac{2mE^{(3)}}{\hbar^2}$$

Both of these equations are similar to the Schrodinger equation in the infinitely deep potential well and have the same boundary conditions too. The standard boundary condition of the wavefunction being continuous at the walls of the box implies that the product of $\psi^{(2)}(y)$ and $\psi^{(3)}(z)$ must vanish at the walls. These boundary conditions when applied to (11a) and (11b) give normalized eigen functions as

$$\psi_{n_y}^{(2)}(y) = \sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right);\ n_y = 1,2,3\ldots$$

and

$$\psi_{n_z}^{(3)}(z) = \sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi z}{c}\right);\ n_z = 1,2,3\ldots$$

Therefore,

$$\psi_{(n_y,\,n_z)}^{(2,\,3)} = \sqrt{\frac{4}{bc}}\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right) \quad \ldots (12)$$

As is clear from (12), the quantum states in a quantum wire are described by two principal quantum numbers n_y and n_z. The energy levels of a quantum wire are given by

$$\left.\begin{aligned} E_{n_y} &= \frac{\pi^2\hbar^2 n_y^2}{2mb^2},\ n_y = 1,2,3,\ldots \\ \text{and}\quad E_{n_z} &= \frac{\pi^2\hbar^2 n_z^2}{2mc^2},\ n_z = 1,2,3,\ldots \end{aligned}\right\} \quad \ldots (13)$$

The energy associated with particle motion in free direction (*i.e.*, x-) is

$$E(k_x) = \frac{\hbar^2 k_x^2}{2m} \quad \ldots(14)$$

Thus, total energy of the particle in a quantum wire is given by

$$E_{(n_y, n_z)}(k_x) = \frac{\hbar^2 k_x^2}{2m} + \frac{\pi^2 \hbar^2 n_y^2}{2mb^2} + \frac{\pi^2 \hbar^2 n_z^2}{2mc^2} \quad ...(15)$$

Thus, the energy of the particle along the confinement directions (y and z) is discrete whereas it can have any value along unconfined (or free) direction (*i.e.*, along x -axis). Total energy of the particle in a quantum wire is not discrete. Further, the eigen energy in a quantum wire increases for decreasing size and a lower effective mass results in a larger eigen energy for a given size of the box.

The applications of nanowires are due to the fact that besides exhibiting quantum confinement effects, nanowire materials are at the same time in the shape of wires. So making electrical connections to the outside world and assembling actual devices may be a lot easier than with other nanostructures, such as quantum dots or quantum wells.

Crossed nanowire junctions have been made, using *p*-type and *n*-type nanowires. These may be used as diodes, or memory elements or as electro luminescent devices (LEDs or Solar Cells). Nanowires have also been used as sensors for monitoring changes in the conductance experienced when different compounds or gases are adsorbed to the surface of the nanowire. Thus, in future, nanowires may serve as efficient sensors for minute amounts of toxic gases, chemical weapons and explosives.

3.9. QUANTUM DOTS

It is a zero dimensional nano-structure in which there is confinement of the particle along all the three directions. The particle is not free to move in any direction. Quantum dots have their radii in the typical range of 2 to 10 nm. Quantum dots can be formed by lithography and etching if a quantum well sample is etched to leave pillars rather than wires as shown in Fig. 3.15.

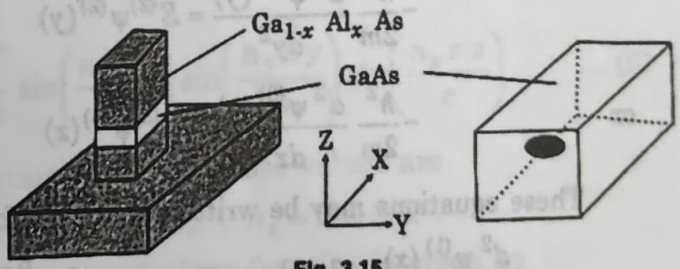
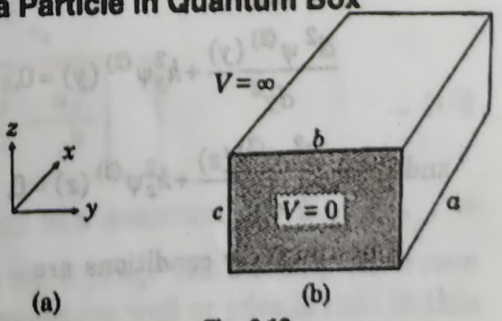


Fig. 3.15.

3.9.1. Application of Schroedinger Equation to a Particle in Quantum Box

Let us discuss the problem of quantum dot from confinement point of view. We consider a cuboid quantum dot or quantum box as shown in Fig. 3.16(b). Spherical quantum dots require numerical solution of Schroedinger equation. The quantum box is a generalization of a quantum wire of rectangular cross-section in which there is additional confinement along



(a) (b)

Fig. 3.16.

the x-direction such that $0 < x < c$. Thus, the particle has no degrees of freedom in momentum and it is now localized in all the three directions. Hence, it has discrete energy states associated with all the three directions of motion.

Let the potential be zero inside the quantum box but infinite everywhere else i.e.,

$$V(x,y,z) = \begin{cases} 0 & \text{for } 0 < x < a, 0 < y < b \text{ and } 0 < z < c \\ \infty & \text{otherwise} \end{cases} \quad \ldots (1)$$

Three dimensional time independent Schroedinger equation within the box ($V = 0$), is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z) \quad \ldots (2)$$

The wave function may be written as a product

$$\psi(x,y,z) = \psi^{(1)}(x)\psi^{(2)}(y)\psi^{(3)}(z) \quad \ldots (3)$$

and the energy can be written as a sum

$$E = E^{(1)} + E^{(2)} + E^{(3)} \quad \ldots (4)$$

where $E^{(1)}, E^{(2)}, E^{(3)}$ are particle energies along x, y and z directions respectively.

Using (3) and (4) in equation (2), which then separates into three equations as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(1)}(x)}{dx^2} = E^{(1)}\psi^{(1)}(x) \quad \ldots (5a)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(2)}(y)}{dy^2} = E^{(2)}\psi^{(2)}(y) \quad \ldots (5b)$$

or

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(3)}(z)}{dz^2} = E^{(3)}\psi^{(3)}(z) \quad \ldots (5c)$$

These equations may be written in simple form as

$$\frac{d^2\psi^{(1)}(x)}{dx^2} + k_x^2\psi^{(1)}(x) = 0, \qquad k_x^2 = \frac{2mE^{(1)}}{\hbar^2} \quad \ldots (6a)$$

$$\frac{d^2\psi^{(2)}(y)}{dy^2} + k_y^2\psi^{(2)}(y) = 0, \qquad k_y^2 = \frac{2mE^{(2)}}{\hbar^2} \quad \ldots (6b)$$

and

$$\frac{d^2\psi^{(3)}(z)}{dz^2} + k_z^2\psi^{(3)}(z) = 0, \qquad k_z^2 = \frac{2mE^{(3)}}{\hbar^2} \quad \ldots (6c)$$

The boundary conditions are

$$\psi^{(1)}(x)=0 \quad \text{at} \quad x=0 \quad \text{and} \quad x=a$$
$$\psi^{(2)}(y)=0 \quad \text{at} \quad y=0 \quad \text{and} \quad y=b$$
$$\psi^{(3)}(z)=0 \quad \text{at} \quad z=0 \quad \text{and} \quad z=c$$

The normalized plane wave solutions of above equations on using boundary conditions of continuity of wave functions at the walls of the box, are

$$\psi^{(1)}_{n_x}(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right) \qquad \ldots (7a)$$

$$\psi^{(2)}_{n_y}(y)=\sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right) \qquad \ldots (7b)$$

and

$$\psi^{(3)}_{n_z}(z)=\sqrt{\frac{2}{c}}\sin\left(\frac{n_z\pi z}{c}\right) \qquad \ldots (7c)$$

The eigen energies are given by

$$E^{(1)}_{n_x}=\frac{\hbar^2k_x^2}{2m}=\frac{\pi^2\hbar^2n_x^2}{2ma^2} \qquad \ldots(8a), \quad k_x=\frac{n_x\pi}{a}$$

$$E^{(2)}_{n_y}=\frac{\hbar^2k_y^2}{2m}=\frac{\pi^2\hbar^2n_y^2}{2mb^2} \qquad \ldots(8b), \quad k_y=\frac{n_y\pi}{b}$$

$$E^{(3)}_{n_z}=\frac{\hbar^2k_z^2}{2m}=\frac{\pi^2\hbar^2n_z^2}{2mc^2} \qquad \ldots(8c) \quad k_z=\frac{n_z\pi}{c}$$

Thus, the complete eigen functions of a quantum dot or a particle in quantum box are

$$\psi_{n_x,n_y,n_z}(x,y,z)=\sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right) \qquad \ldots (9)$$

which involves three principal quantum numbers whose values are

$$n_x=1,2,3,\ldots; \quad n_y=1,2,3,\ldots; \quad n_z=1,2,3,\ldots .$$

Also the eigen energy corresponding to an eigen function is given by

$$E_{n_x,n_y,n_z}=E^{(1)}_{n_x}+E^{(2)}_{n_y}+E^{(3)}_{n_z}$$

or

$$E_{n_x,n_y,n_z}=\frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right) \qquad \ldots (10)$$

As is clear from equation (10), the total energy of a quantum dot, E_{n_x,n_y,n_z}, is discrete depending upon three quantum numbers n_x, n_y, n_z. The striking difference between the case of a quantum dot and that of a quantum well or wire is that in this